LIQUEFACTION OF WASTE LOW DENSITY POLYETHYLENE TO USEFUL PRODUCTS

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
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CERTIFICATE

This is to certify that the thesis entitled, **"LIQUEFACTION OF WASTE LOW DENSITY POLYETHYLENE TO USEFUL PRODUCTS"** submitted by Mr. Ashish Sharma in partial fulfilments for the requirements for the award of Bachelor of Technology Degree in Chemical Engineering at National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

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Date: 13/05/2010 **ASHISH SHARMA**

ABSTRACT

The degradation of waste LDPE sample was carried out in the temperature range of 475-600^{0}C by both thermal degradation and by catalytic degradation using SILICA-ALUMINA as catalyst. It was found that liquid product yield increases with increasing temperature in both thermal as well as catalytic degradation till 550^{0}C; the time taken for the pyrolysis also decreases when we use catalyst, afterwards liquid product yield starts decreasing with increasing temperature. In the second phase the LDPE was pyrolysed with catalyst in varying proportions such as 4:1 and 8:1 the product yield increased in the first case while decreasing in the latter detailed FT-IR spectroscopy of the liquid products was done showing the presence of different functional groups. The results obtained from the FT-IR spectroscopic analysis were found in almost complete agreement with the standard GC-MS analysis of the liquid product obtained from the pyrolysis of LDPE. The yield of product was max at 550^{0}c with catalyst in ratio 4:1.

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CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

In 1868, a young American printer, named John Wesley Hyatt, was searching for a new material to be used as a substitute for ivory in the making of billiard balls.

This new plastic was called *Bakelite*. Many new plastics have been made since Bakelite. Production of plastics has increased over 2000% since Bakelite was first produced, and there are now more than twenty known types. Research along the lines of plastics has given a great impetus to research and invention in many other different fields of endeavour. Millions of dollars are spent yearly in plastics research, trying to find new plastics and to improve the existing ones. Much research will be done in the future to lower the cost of producing plastics so that their consumption will become greater. It seems safe to say that if the application and use of plastics continue to increase at the present rate, we may be living in a "Plastics Age."

The major chemicals used to make plastic resins pose serious risks to public health and safety. Many of the chemicals used in large volumes to produce plastics are highly toxic. Some chemicals, like *benzene* and *vinyl chloride*, are known to cause cancer in humans; many tend to be gases and liquid hydrocarbons, which readily vaporize and pollute the air. Many are flammable and explosive. Even the plastic resins themselves are flammable and have contributed to numerous chemical accidents. The production of plastic emits substantial amounts of toxins (e.g. *ethylene oxide, benzene* and *xylenes*) to air and water. Many of the toxic chemicals released in plastic production can cause cancer and birth defects and damage the nervous system, blood, kidneys and immune systems. These chemicals can also cause serious damage to ecosystems.

The disposal of municipal solid waste (MSW) causes serious concern over environmental issues in our world. There are several methods for disposal of MSW and plastic waste, i.e., landfilling, incineration, recycling, and chemical recovery. For recycling, thermal degradation of plastic

waste has an important role in dealing with the enormous amounts of plastic waste produced. It is attracting great interest because it offers the possibility of recovering energy and useful chemicals. It is also a general way of breaking polymers down to their constituent monomers, which in turn can be used again in refineries or in petrochemical and chemical production.

Thermal degradation technologies are currently being explored and include, e.g., pyrolysis, hydrogenation, gasification, and thermal cracking. Pyrolysis of polymeric materials has long been a subject of investigation, and it is currently attracting increased interest in the context of recovery of valuable products from polymeric waste. The pyrolysis processes consist of the thermal degradation of wastes in the absence of oxygen or air.

Fig.1.1 some household products made from LDPE

1.2 LOW DENSITY POLYETHYLENE (LDPE)

The first of the polyolefins, Low Density Polyethylene (LDPE) was originally prepared some fifty years ago by the high pressure polymerization of ethylene. Its comparatively low density arises from the presence of a small amount of branching in the chain (on about 2% of the carbon atoms). This gives a more open structure. Low Density Polyethylene (LDPE) is a most useful and widely used plastic especially indispensing bottles or wash bottles.

It is translucent to opaque, robust enough to be virtually unbreakable and at the same time quite flexible. Chemically LDPE is unreactive at room temperature although it is slowly attacked by strong oxidizing agents and some solvents will cause softening or swelling. It may be used at temperatures up to 95°C for short periods and at 80°C continuously. LDPE is ideally suited for a wide range of molded laboratory apparatus including wash bottles, pipette washing equipment, general purpose tubing, bags and small tanks.It has "4" as its recycling symbol.

Fig.1.2 recycling code of LDPE

1.3 GRADING OF PLASTICS WITH RECYCLING CODES

NUMBER 1 PLASTICS – PET OR PETE (POLYETHYLENE TEREPHTHALATE)

1st Life: Soda, water and beer bottles; mouthwash bottles; peanut butter containers; salad dressing and vegetable oil containers; etc.
Recycling: Picked up through most curbside recycling programs.
2nd Life: Polar fleece fiber, tote bags, furniture, carpet, paneling, and occasionally made into new plastic containers

NUMBER 2 PLASTICS – HDPE (HIGH DENSITY POLYETHYLENE)

1st Life: Milk jugs, juice bottles; bleach, detergent and household cleaner bottles; shampoo bottles; some trash and shopping bags; motor oil bottles; cereal box liners; etc.

Recycling: Picked up through most curbside recycling programs.
2nd Life: Detergent bottles, recycling containers, floor tile, drainage pipe, benches, picnic tables, fencing

NUMBER 3 PLASTICS – PVC (POLYVINYL CHLORIDE)

1st Life: Window cleaner and detergent bottles, shampoo bottles, clear food packaging, wire jacketing, medical equipment, siding, windows, piping; etc.
Recycling: Rarely recycled because collecting it for recycling is cost-prohibitive. There are not enough items made from the material to warrant factories to recycle it into new products; however some plastic lumber makers will now accept it.
2nd Life: Decks, paneling, mud flaps, roadway gutters, flooring, cables, speed bumps, mats

NUMBER 4 PLASTICS – LDPE (LOW DENSITY POLYETHYLENE)

1st Life: Squeezable bottles; bread, dry cleaning and shopping bags; tote bags; carpet; etc.
Recycling: Rarely picked up through curbside programs, however some stores will accept plastic shopping bags for recycling.
2nd Life: Trash can liners and cans, compost bins, shipping envelopes, paneling, lumber, floor tile

NUMBER 5 PLASTICS – PP (POLYPROPYLENE)

1st Life: Syrup bottles, ketchup bottles, caps, straws, medicine bottles, diapers; etc.
Recycling: Picked up through most curbside recycling programs.
2nd Life: Battery cables, brooms, brushes, auto battery cases, ice scrapers, landscape borders, bicycle racks, rakes, bins

NUMBER 6 PLASTICS – PS (POLYSTYRENE)

1st Life: Disposable plates and cups, meat trays, egg cartons, carry-out containers, aspirin bottles, compact disc cases; etc.

Recycling: Picked up through some curbside recycling programs.
2nd Life: Insulation, light switch plates, egg cartons, vents, rulers, foam packing, carry-out containers

NUMBER 7 PLASTICS – OTHER

1st Life: 3 and 5 gallon water bottles, 'bullet-proof' materials, sunglasses, DVDs, iPod and computer cases, signs and displays, nylon; etc.
Recycling: Not traditionally recycled, however some curbside programs now take them.
2nd Life: Plastic lumber, custom-made products

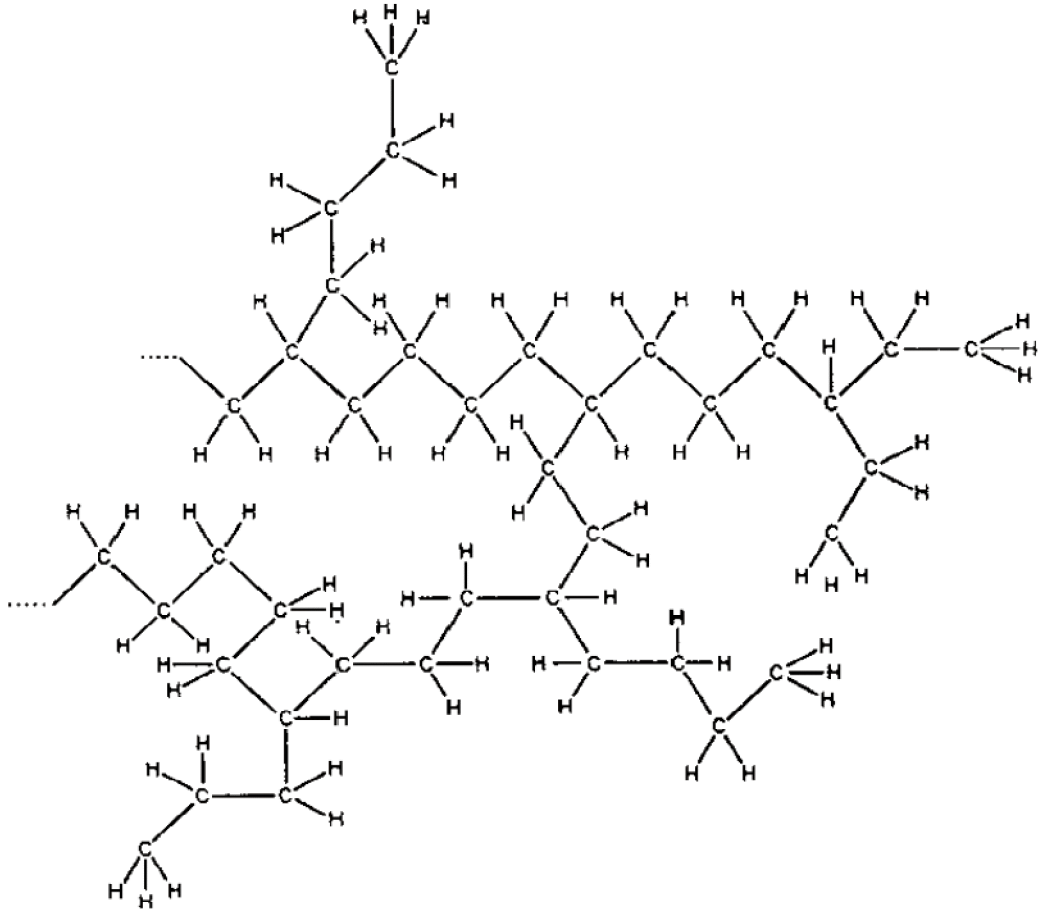


Fig.1.3 simulated structural formula of branched low-density polyethylene [1]

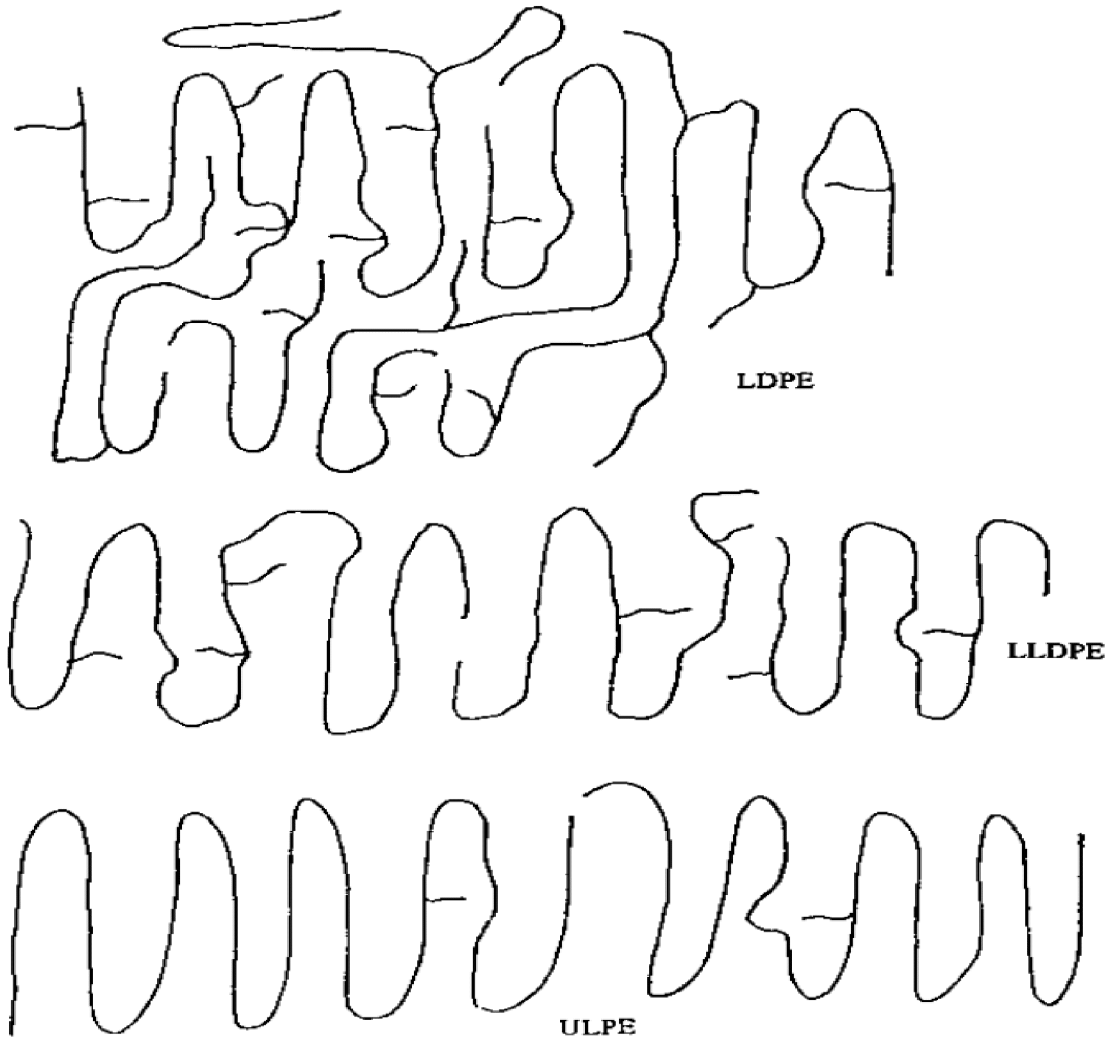


Fig.1.4 different kinds of plastics in comparison with LDPE [1]

1.4 MANUFACTURE OF LDPE

Polymerization of ethylene can be done according to three mechanisms:

1) *Free radical polymerization yielding LDPE.* Polymeric chains are branched allowing the material to have specific performances (rheology and mechanical properties).

2) *Ziegler Natta catalysis of HDPE or LLDPE by addition of co-monomers*. Macromolecules are linear with some short branched segments.

3) *Metallocene catalysis* yields linear and tailored structures leading to formation of special resins.

There are two main processes by which LDPE is produced via free radical chemistry:

→ The tubular process

→ The autoclave process

Table 1.1 COMPARISON OF CHARACTERISTICS OF TUBULAR AND AUTOCLAVE PROCESS

	TUBULAR PROCESS	**AUTOCLAVE PROCESS**
Reactor volume (m3)	0.6-10	0.4-2.3
Reactor design	Tube hundreds of meters Inner diameter < 5cm	Multi-zone reactor, continuous stirring
Reactor cooling	yes	no
Monomer injection	mono or multi-injection	mono or multi-injection
Oxygen as initiator	yes	no
Peroxides as initiators	yes	yes
Peroxide injection	mono or multi-injection	multi-injection
Residence time(s)	20-80	20-80
Pressure (bar)	2200-2700	1300-2200
Temperature (°C)	130-325	160-310
Monomer conversation (%)	15-30	15-20

The reaction takes place at temperatures between 100 to 300°C and at high pressure (1200-3000 bars). At these pressures ethylene liquefies and acts as a solvent under supercritical conditions.

Molecular weight and density is regulated by controlling the temperature and pressure, and by the addition of a chain transfer agent (e.g. propane).

The selection of the right organic peroxide is a critical parameter to consider for LDPE polymerization. The "initiator package" affects directly the polymer properties and also the productivity (% conversion, Cost /kg of monomer converted).

1.5 MECHANISM OF POLYMERISATION

Polymers, called macromolecules, are made up of many repeating subunits (monomers) by polymerization reactions.

Polyethylene has been produced commercially since 1943.

1) PE is used in manufacturing flexible bottles, films, sheets, and insulation for electric wires.

2) PE produced by radical polymerization has a softening point of about 110°C.

PE can be produced using Ziegler-Natta catalysts (organometallic complexes of transition metals) in which no radicals are produced, no back biting occurs, and, consequently, there is no chain branching [2].

Chain-growth polymers (addition polymers):

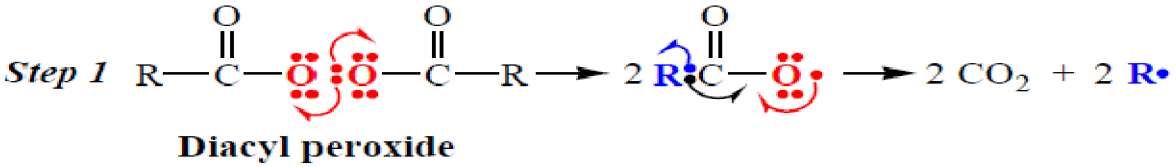
1) Ethylene polymerizes by a radical mechanism when it is heated at a pressure of 1000 atm with a small amount of an organic peroxide.

2) The polyethylene is useful only when it has a molecular weight of nearly 1,000,000.

3) Very high molecular weight polyethylene can be obtained by using a low concentration of the initiator ⇒ initiates the polymerization of only a few chains and ensures that each will have a large excess of the monomer available [2].

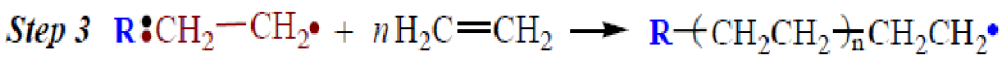
Radical Polymerization of Ethene

Chain Initiation



The diacyl peroxide dissociates to produce radicals, which in turn initiate chains.

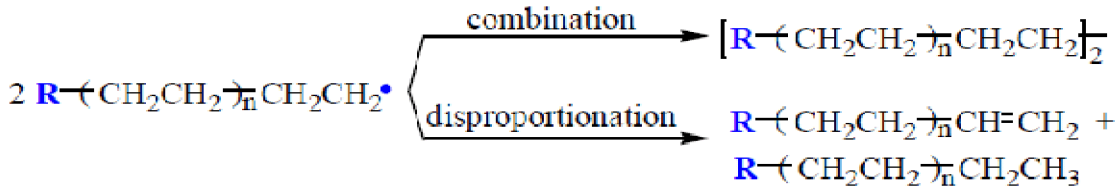
Chain Propagation



Chain propagation by adding successive ethylene units, until their growth is stopped by combination or disproportionation.

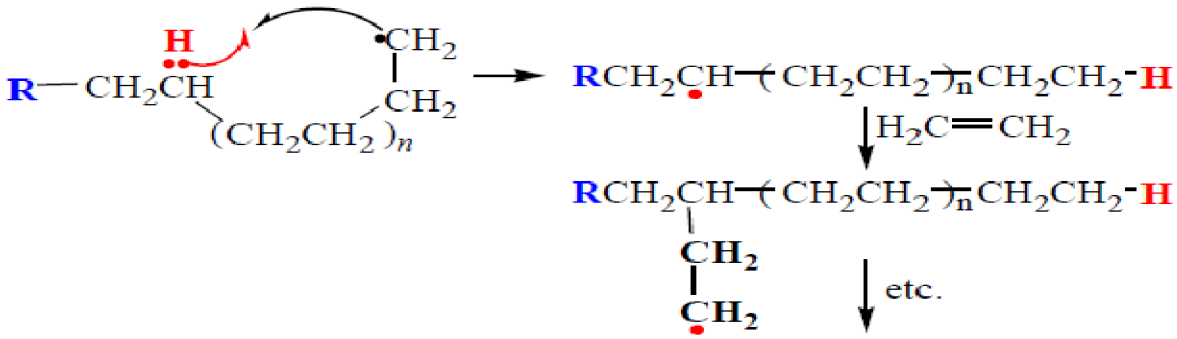
Chain Termination

Step 4



The radical at the end of the growing polymer chain can also abstract a hydrogen atom from itself by what is called "back biting." This leads to chain branching [2].

Chain Branching



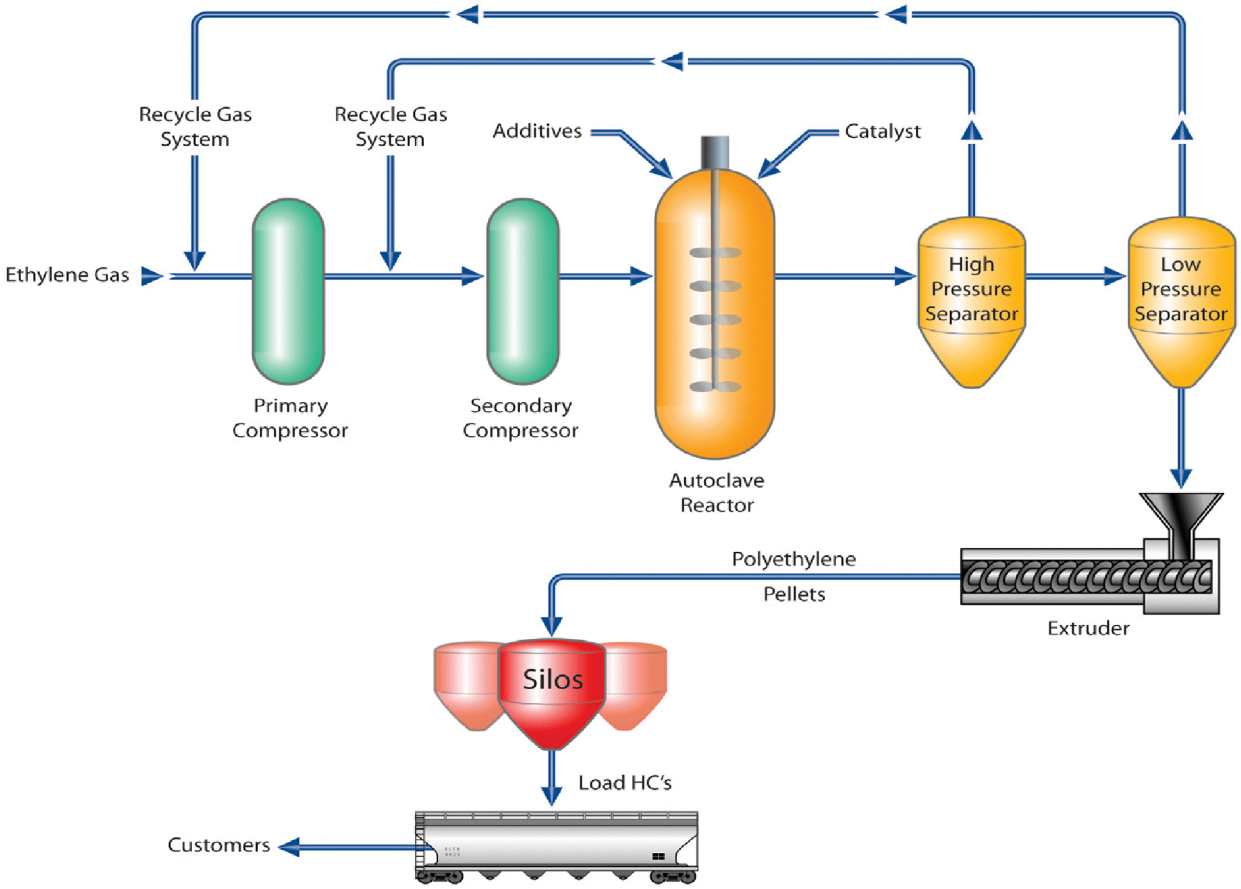


Fig.1.5 LDPE production process diagram

Table 1.2 PROPERTIES OF LDPE

Mechanical Properties

Quantity	Value	Unit
Young's modulus	200 - 400	MPa
Shear modulus	100 - 350	MPa
Tensile strength	8 - 12	MPa
Elongation	600 - 650	%
Bending strength	10 - 40	MPa
Yield strength	15 - 20	MPa

Physical Properties

Quantity	Value	Unit
Thermal expansion	150 - 200	e-6/K
Thermal conductivity	0.3 - 0.335	W/m.K
Specific heat	1800 - 3400	J/kg.K
Melting temperature	125 - 136	°C
Glass temperature	-110 - -110	°C
Service temperature	-30 - 70	°C
Density	910 - 928	kg/m3
Resistivity	5e+17 - 1e+21	Ohm.mm2/m
Breakdown potential	17.7 - 39.4	kV/mm
Dielectric loss factor	0.0002 - 0.001	
Friction coefficient	0.3 - 0.5	
Refraction index	1.51 - 1.53	
Shrinkage	1.5 - 3	%
Water absorption	0.005 - 0.015	%

Environmental Data

Quantity	Value	Unit
Eco indicator 95	3.301	mPt
EPS	840	mELU
Ex (in) / Ex (out)	1.99762213575443	MJ/MJ
GER	83.41	MJ
Raw materials input	71.2330124908	kg
Solid	0.0042100376	kg
Eco indicator 99	0.374	Pt

Chemical Properties

Excellent resistance (no attack) to dilute and concentrated acids, alcohols, bases and esters.

1. Good resistance (minor attack) to aldehydes, ketones and vegetable oils.
2. Limited resistance (moderate attack suitable for short-term use only) to aliphatic and aromatic hydrocarbons, mineral oils, and oxidizing agents.
3. Poor resistance, and not recommended for use with Halogenated hydrocarbons.

1.7 APPLICATIONS

LDPE is widely used for manufacturing various containers, dispensing bottles, wash bottles, tubing, plastic bags for computer components, and various molded laboratory equipment. Its most common use is in plastic bags. Other products made from it include:

- Food storage and laboratory containers.
- Corrosion-resistant work surfaces.
- Parts that need to be weldable and machinable.
- Parts that require flexibility, for which it serves very well.
- Very soft and pliable parts.
- Six-pack soda can rings.
- Juice and milk cartons, whose "cardboard" is actually liquid packaging board, a laminate of paperboard and LDPE (as the water-proof inner and outer layer), and often with of a layer of aluminium foil (thus becoming aseptic packaging).
- Computer components, such as hard drives, screen cards and disk-drives.
- Playground Slides.
- Plastic Bags.
- Plastic Wraps.

CHAPTER 2

LITERATURE REVIEW

PYROLYSIS OF LDPE TO USEFUL CHEMICALS

2.1 WORKS DONE ON LDPE PYROLYSIS BY DIFFERENT INVESTIGATORS

1) ***Low temperature conversion of plastic waste into light hydrocarbons***

Advance recycling through pyrolytic technology has the potential of being applied to the management of plastic waste (PW). For this purpose 1 Lt volume, energy efficient batch reactor was manufactured locally and tested for pyrolysis of waste plastic. The feedstock for reactor was 50 g waste polyethylene. The average yield of the pyrolytic oil, wax, pyrogas and char from pyrolysis of PW were 48.6, 40.7, 10.1 and 0.6%, respectively, at 275^{0}C with non-catalytic process. Using catalyst the average yields of pyrolytic oil, pyrogas, wax and residue (char) of 50 g of PW was 47.98, 35.43, 16.09 and 0.50%, respectively, at operating temperature of 250^{0}C. The designed reactor could work at low temperature in the absence of a catalyst to obtain similar products as for a catalytic process. [3]

2) ***Catalytic pyrolysis of low-density polyethylene with lead sulfide into fuel oil***

The influence of lead sulfide as a catalyst on the pyrolysis of low-density polyethylene has been investigated. The yield and composition of the derived gas, oil and wax have been studied in terms of the temperature, time and amount of catalyst. The oil consisted of mainly paraffins and olefins. More than 70% yield of gas and liquid fraction with boiling point up to 350^{0}C was obtained. The composition of the oil fraction was characterized by physicochemical properties of petroleum fuel. Distillation data showed that ~10% have the boiling range of light naphtha (<160 ^{0}C), ~30% of heavy naphtha (160-208^{0}C) and ~55% of middle distillate (208-350^{0}C). Lead sulfide was found to be an effective catalyst for conversion of polyethylene into fuel oil. [4]

3) ***A comparative study of liquid product on non-catalytic and catalytic degradation of waste plastics using spent FCC catalyst***

Non-catalytic and catalytic degradation of waste plastics (high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP) and polystyrene (PS)) using spent fluid catalytic cracking (FCC) catalyst into liquid product were comparatively studied with a stirred semi-batch reactor at 400^0C, under nitrogen stream. Liquid product characteristics were described by cumulative distribution as a function of lapse time of reaction, paraffin, olefin, naphthene and aromatic (PONA) composition, and also carbon number distribution on plastic type of reactant. For degradation of waste PE with relatively high degradation temperature, the effect of adding spent FCC catalyst greatly appeared on cumulative distribution of liquid product with a reaction lapse time, whereas those for waste PP and PS with low degradation temperature showed a similar trend in both non-catalytic and catalytic degradation at 400^0C. In PONA and carbon number distribution of liquid product, the characteristics of waste PS that was mainly degraded by end chain scission mechanism were not much altered in presence of spent FCC catalyst. However, waste polyolefinic polymer that was degraded by a random chain scission mechanism significantly differed on PONA and carbon number distribution of liquid product with or without spent FCC catalyst. The addition of spent FCC catalyst in degradation of polyolefinic polymer, which economically has a benefit in utilization of waste catalyst, significantly improved the light olefin product by its high cracking ability and also the aromatic product by cyclization of olefin as shape selectivity in micropore of catalyst [5].

4) ***The catalytic performance for LDPE destruction over aluminum-incorporated mesoporous silicates***

The aim of this study was to investigate the aluminum-incorporated mesoporous silicate (Al-MPS) as a thermal catalyst for the destruction of low density polyethylene (LDPE). Various Al-MPS (Si/Al molar ratios = 117.6, 58.8, 39.2 and 29.4) materials were successfully synthesized without any structural damage. With regard to the X-ray diffraction (XRD) pattern, the main peak of 2u = 64.0 in Al2O3 did not show until the incorporation of Si/Al = 58.8. This result implies the aluminum ions were stably substituted into the silicon site of the mesoporous framework. The hexagonal straight pore size increased to about 8.0 nm in Al (Si/Al = 58.8)-MPS, but then decreased in the range of 3.0–5.0 nm in Al (Si/ Al = 29.4)-MPS. In relation to the

amount of incorporated aluminum, the Al-MPS absorbed many pyridine molecules, implying the acidities on the external surfaces up to Si/Al = 58.8, but this amount decreased somewhat above a Si/Al ratio of 39.2. The catalytic decomposition of LDPE was enhanced in Al (Si/Al = 58.8)-MPS and particularly, the selectivity to light hydrocarbons below C4 reached 43% [6].

5) ***Pyrolysis of low-density polyethylene using synthetic catalysts produced***

From fly ash Catalytic pyrolysis of low-density polyethylene (LDPE) was investigated using various fly ash-derived silica–alumina catalysts (FSAs). FSAs were prepared by a simple activation method that basically includes NaOH treatment of fly ash by a fusion method, followed by an aging process. A series of LDPE pyrolysis experiments was conducted and the catalytic performance of FSAs was assessed in terms of the degradation temperature and the simulated boiling point distribution of the liquid products. The effects of synthesis conditions such as NaOH/fly ash weight ratio and aging time were examined by X-ray diffractometer (XRD), Brunauer-Emmett-Teller (BET) surface area analyzer, and scanning electron microscope to clarify the controlling factors affecting the catalytic activity. To obtain catalyst with high activity, it is necessary to produce sufficient silica and alumina species that can be easily co-precipitated into solid acid catalyst by destruction of the fly ash structure and to optimize the activation time for catalyst synthesis to prevent the transformation into inactive phases. The catalytic performance of FSA obtained from optimal conditions was equivalent to that of commercial catalysts, demonstrating the effectiveness of the catalyst [7].

CHAPTER 3

EXPERIMENTAL PROCEDURE

THERMAL AND CATALYTIC PYROLYSIS OF LDPE IN BATCH REACTOR

3.1 SAMPLE PREPARATION

1) The raw material as plastic bags was procured from the market.
2) The raw material is shrunk by applying heat and cut down to small pieces so that to increase the surface area.
3) This material is now subjected to pyrolysis.

3.2DESCRIPTION OF THE EXPERIMENTAL SET-UP

The experimental set-up is composed of three main parts:
1) Reactor
2) Furnace
3) Condenser

REACTOR

It is a stainless steel tube of length 145 mm, internal diameter 37 mm and outer diameter 41 mm sealed at one end and an outlet tube at other end. The rector is to be placed inside the furnace for external heating with the raw material in side it for external heating.

Fig.3.1 reactor

FURNACE

The furnace provides the heating in the set-up the rector is to be heated inside it for the pyrolysis to be carried out it has a Cr-Al k type thermocouple to control the temperature it is also connected to a PID controller.

CONDENSER

This equipment does all the work outside the furnace where the actual pyrolysis is taking place it cools down and collects the heated vapours coming out of the outlet tube of the reactor. It has an inlet and an outlet for cold water to run through its outer area this is used for cooling of the vapours.

Fig.3.2 experimental set-up

3.3 PYROLYSIS PROCEDURE

15 gms of the sample prepared earlier is stuffed inside the reactor and the reactor is placed inside the furnace for heating ,this what we do in case of thermal pyrolysis , in case of catalytic cracking we also add silica –alumina catalyst along with sample in suitable ratios with it .The temperature is set on the PID controller for the pyrolysis to take place we note down the reaction start temp as the one when first drop of liquid comes out of the reactor outlet tube the pyrolysis continues slowly or rapidly depending on the temp and the proportion of catalyst being used by us .

The condensed liquid is collected in a measuring cylinder it is weighted. The weight of the waxy residue left inside the reactor is also taken now the weight of the gaseous products that escaped can be calculated using material balance assuming to weight loss during the pyrolysis.

The suitable temperatures at which the pyrolysis is to be performed is understood with the help of a TGA analysis

3.4 THERMO-GRAVIMETRIC ANALYSIS

Thermo-gravimetric analysis or thermal gravimetric analysis (TGA) is a type of testing that is performed on samples to determine changes in weight in relation to change in temperature. Such analysis relies on a high degree of precision in three measurements: weight, temperature, and temperature change. As many weight loss curves look similar, the weight loss curve may require transformation before results may be interpreted. A derivative weight loss curve can be used to tell the point at which weight loss is most apparent. Again, interpretation is limited without further modifications and deconvolution of the overlapping peaks may be required.

TGA is commonly employed in research and testing to determine characteristics of materials such as polymers, to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points of explosives, and solvent residues. It is also often used to estimate the corrosion kinetics in high temperature oxidation. Simultaneous TGA-DTA/DSC measures both heat flow and weight changes (TGA) in a material as a function of temperature or time in a controlled atmosphere. Simultaneous measurement of these two material properties not only improves productivity but also simplifies interpretation of the results. The complementary information obtained allows differentiation between endothermic and exothermic events which have no associated weight loss (e.g., melting and crystallization) and those which involve a weight loss (e.g., degradation).

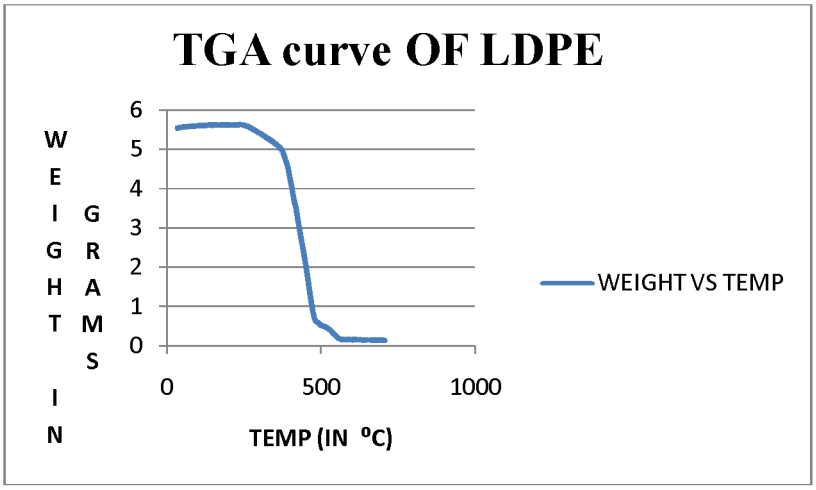


Fig.3.3 TGA curve of LDPE

Fig.3.4 A typical example of a TGA

From the thermo gravimetric analysis curve above of LDPE it is evident that the best temp for the pyrolysis of LDPE is from 475-600^{0}C.

CHAPTER 4

TABULATION

Table 4.1 OBSERVATION TABLE (THERMAL PYROLYSIS)

Thermal pyrolysis of 15 grams of LDPE sample At following temp (°C)	Weight of liquid Products obtained (grams)	Weight of solid Products obtained (grams)	Weight of gaseous Products obtained by difference (grams)	Total time for Thermal pyrolysis (mins)
475	7.1	0.2	7.7	146
500	9.48	0.15	5.37	80
525	10.48	0.37	4.15	65
550	11.56	0.25	3.19	57
575	11.3	0.09	3.61	41
600	10.12	0.55	4.33	37

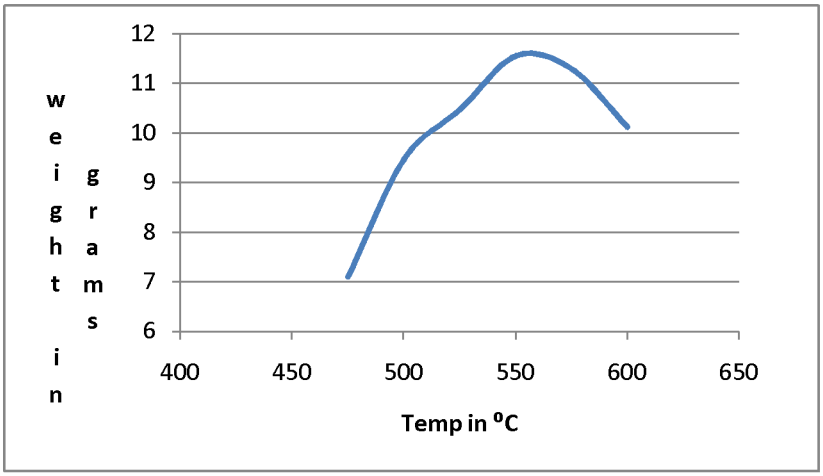


Fig.4.1 plot of weight of liquid product vs. temperature

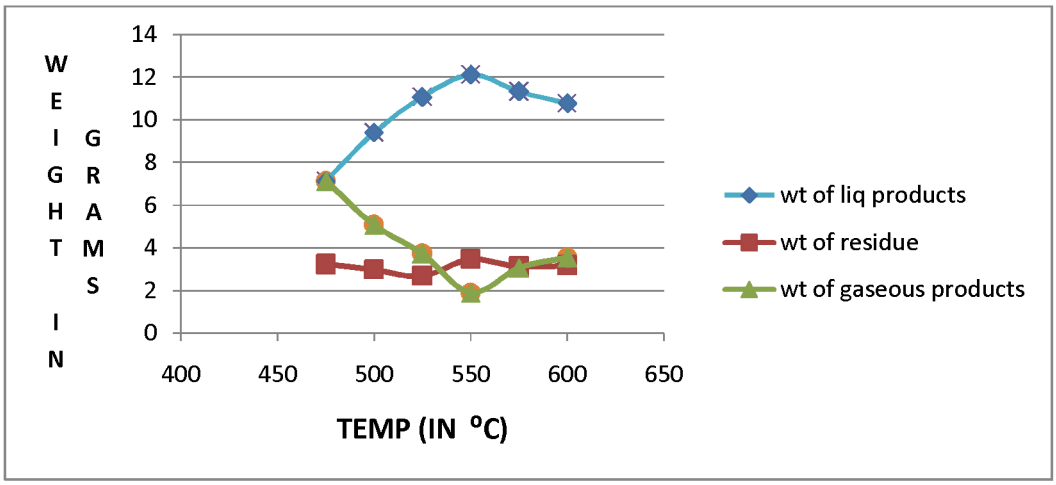


Fig.4.2 common plot for solid, liquid and gaseous products in thermal pyrolysis against temperature

Table 4.2 OBSERVATION TABLE (FOR CATALYTIC PYROLYSIS)

Catalytic pyrolysis of 15 grams of LDPE sample With 2.5 gram silica-alumina at following temp (in ^{0}C),(ratio 6:1)	Weight of liquid Products obtained (in grams)	Weight of solid residue obtained (in grams)	Weight of gaseous Products obtained (grams)	Total time for Thermal pyrolysis (mins)
475	7.13	3.23	7.14	125
500	9.42	2.99	5.09	71
525	11.08	2.68	3.74	61
550	12.12	3.47	1.91	49
575	11.32	3.12	3.06	36
600	10.78	3.17	3.55	30

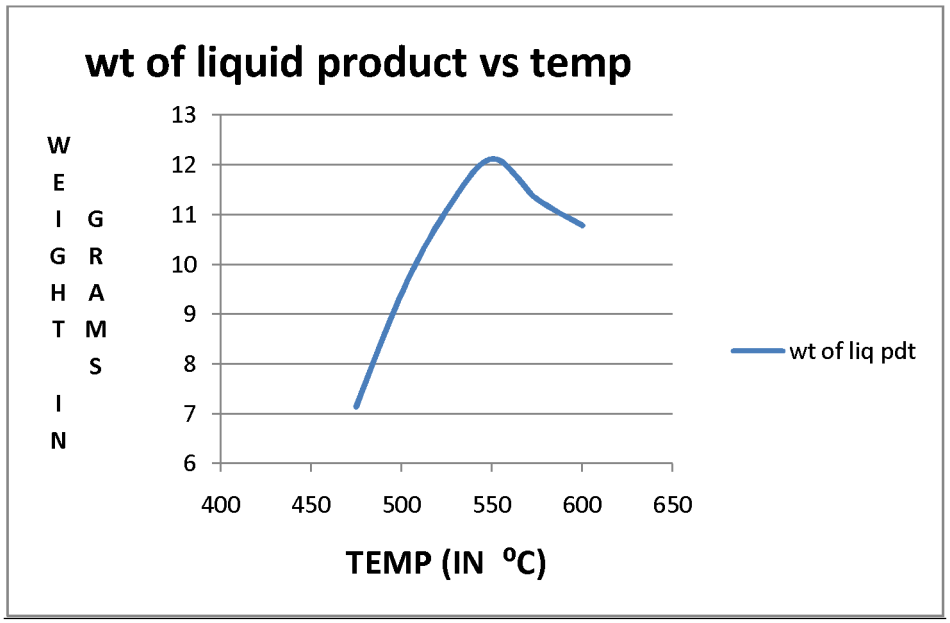


Fig.4.3 plot of weight of liquid product obtained during catalytic pyrolysis of LDPE with Si-Al catalyst (6:1)

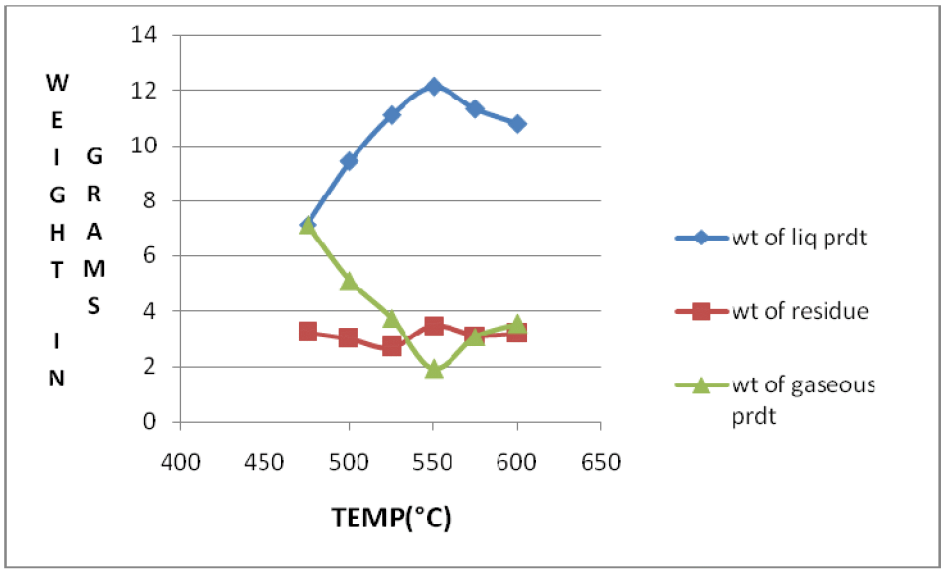


Fig.4.4 plot of liquid, solid and gaseous product obtained in the catalytic pyrolysis of LDPE (6:1) against temperature

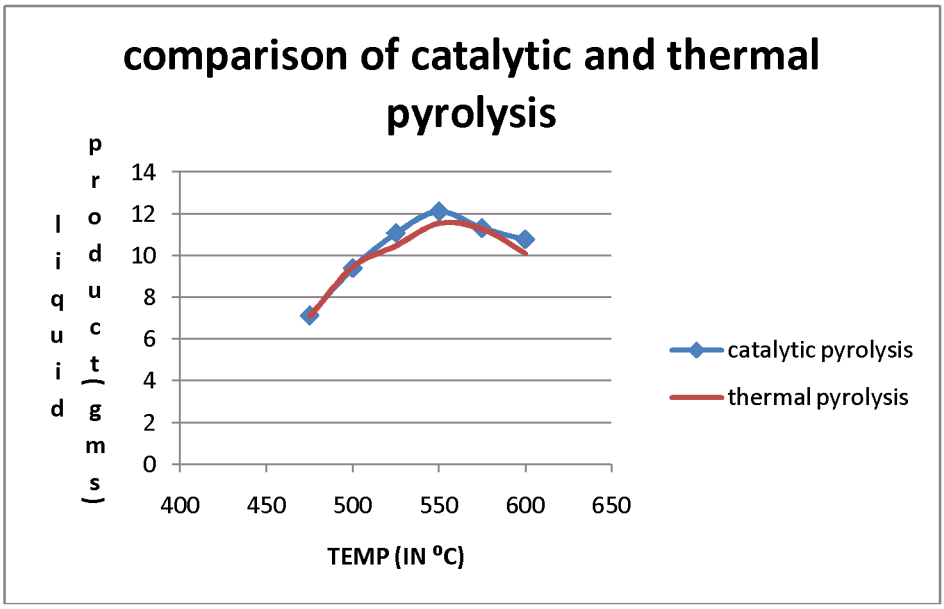


Fig.4.5 Comparative plot of catalytic and thermal pyrolysis

Table 4.3 OBSERVATION TABLE (FOR CATALYTIC PYROLYSIS)

Catalytic pyrolysis of 15 grams of LDPE sample at 550^{0}C with following amount of silica-alumina in grams.	Weight of liquid Products obtained (grams)	Weight of solid Products obtained (grams)	Weight of gaseous Products obtained (grams)	Total time for Thermal pyrolysis (mins)
3.75 (4:1)	12.65	4.08	2.02	42
2.5 (6 : 1)	12.12	3.47	1.91	49
1.875 (8 : 1)	12.04	2.13	2.705	52

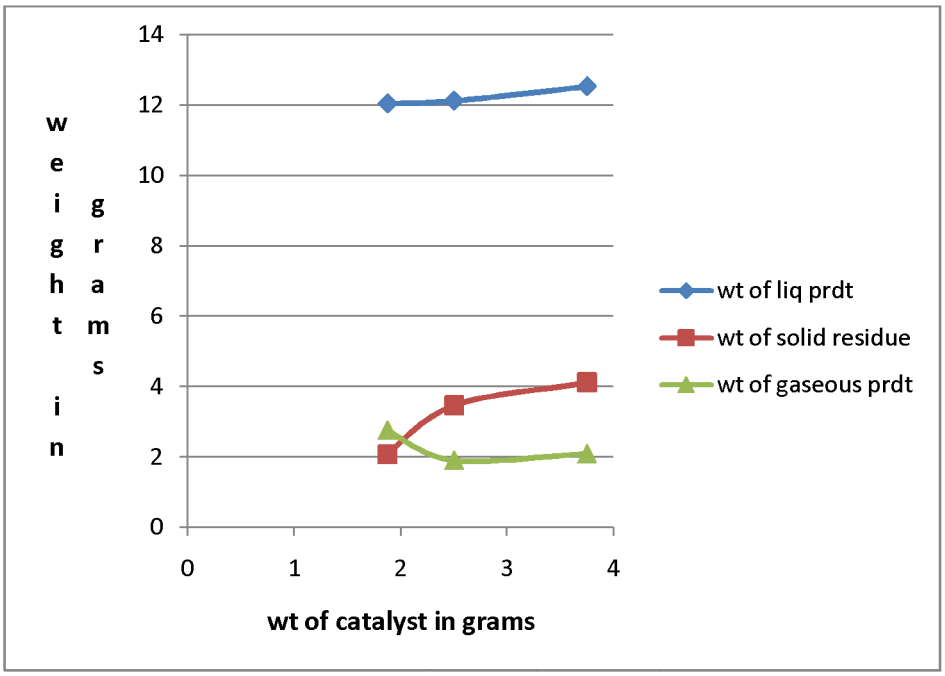


Fig.4.6 plot for comparison of catalytic pyrolysis at different catalyst ratios

4.1 FOURIER TRANSFORM INFRARED SPECTROSCOPY

Infrared spectroscopy (IR spectroscopy) is the subset of spectroscopy that deals with the infrared region of the electromagnetic spectrum. It covers a range of techniques, the most common being a form of absorption spectroscopy. As with all spectroscopic techniques, it can be used to identify compounds and investigate sample composition. A common laboratory instrument that uses this technique is an infrared spectrophotometer.

The infrared portion of the electromagnetic spectrum is usually divided into three regions; the near-, mid- and far- infrared, named for their relation to the visible spectrum. The far-infrared, approximately 400–10 cm−1 (1000–30 μm), lying adjacent to the microwave region, has low energy and may be used for rotational spectroscopy. The mid-infrared, approximately 4000–400 cm−1 (30–2.5 μm) may be used to study the fundamental vibrations and associated rotational-vibrational structure. The higher energy near-IR, approximately 14000–4000 cm−1 (2.5–0.8 μm) can excite overtone or harmonic vibrations. The names and

classifications of these subregions are merely conventions. They are neither strict divisions nor based on exact molecular or electromagnetic properties [8, 9].

4.2 PRACTICAL IR SPECTROSCOPY

The infrared spectrum of a sample is recorded by passing a beam of infrared light through the sample. Examination of the transmitted light reveals how much energy was absorbed at each wavelength. This can be done with a monochromatic beam, which changes in wavelength over time, or by using a Fourier transform instrument to measure all wavelengths at once. From this, a transmittance or absorbance spectrum can be produced, showing at which IR wavelengths the sample absorbs. Analysis of these absorption characteristics reveals details about the molecular structure of the sample. When the frequency of the IR is the same as the vibrational frequency of a bond, absorption occurs.

This technique works almost exclusively on samples with covalent bonds. Simple spectra are obtained from samples with few IR active bonds and high levels of purity. More complex molecular structures lead to more absorption bands and more complex spectra. The technique has been used for the characterization of very complex mixtures [8, 9].

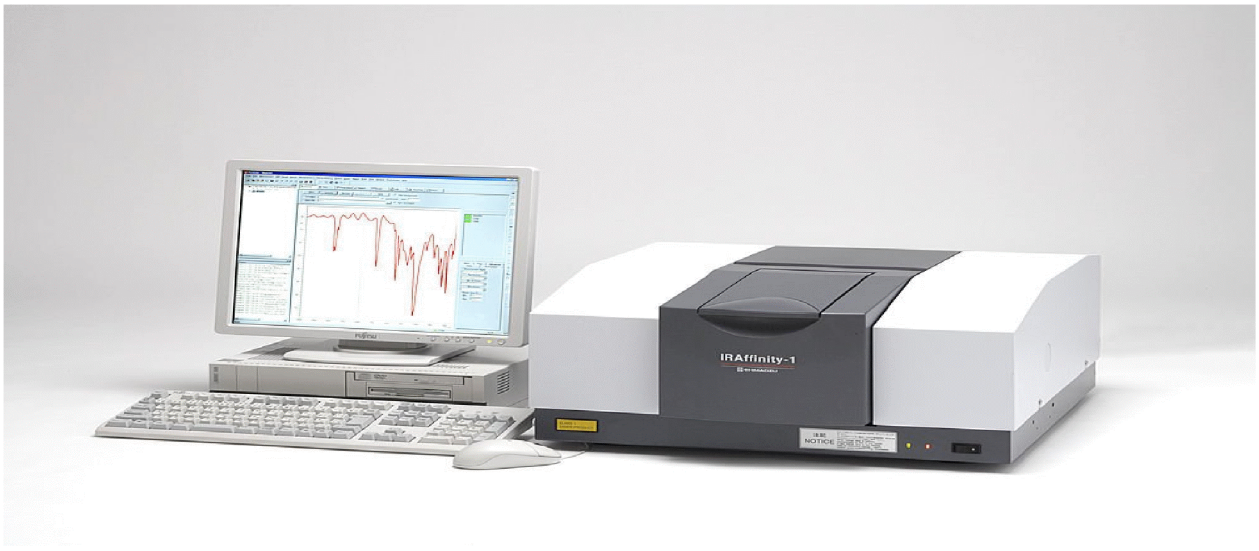


Fig.4.7 A FTIR Spectrometer

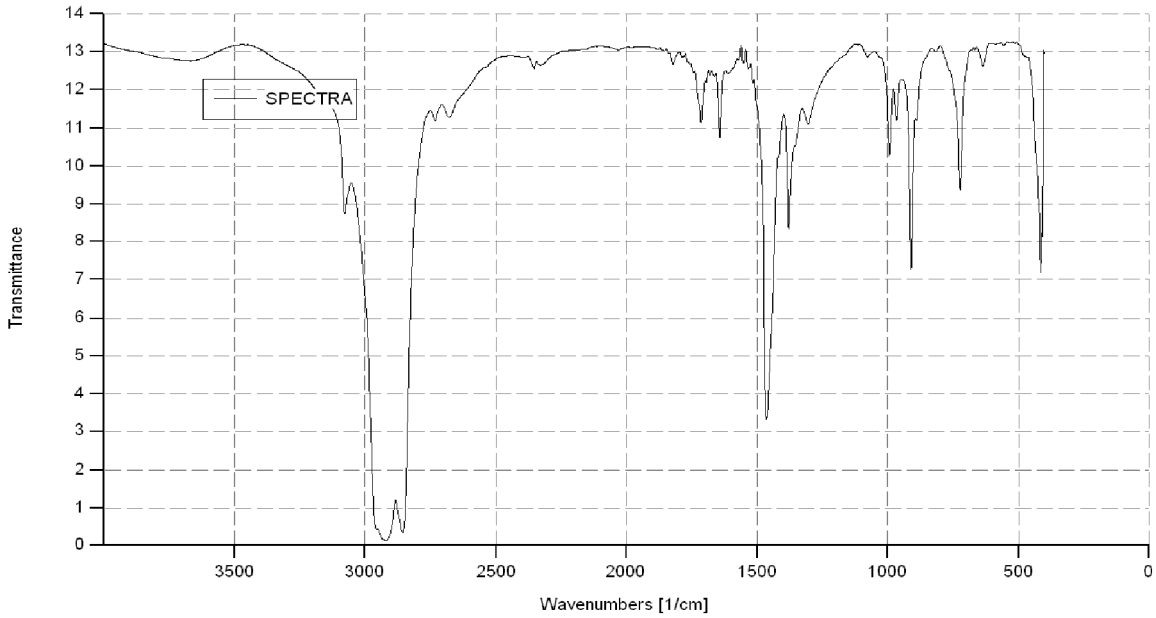


Fig.4.8 FT-IR of the liquid product obtained by the catalytic (silica-alumina) pyrolysis of the waste LDPE sample at 550 ^{0}c

Table 4.4 CHARACTERISTIC ABSORPTION FREQUENCIES FOR DIFFERENT BONDS

CHARACTERISTIC INFRARED ABSORPTION FREQUENCIES

Bond	Compound Type	Frequency range, cm^{-1}
C-H	Alkanes	2960-2850(s) stretch
		1470-1350(v) scissoring and bending
	CH_3 Umbrella Deformation	1380(m-w) - Doublet - isopropyl, *t*-butyl
C-H	Alkenes	3080-3020(m) stretch
		1000-675(s) bend
C-H	Aromatic Rings	3100-3000(m) stretch
	Phenyl Ring Substitution Bands	870-675(s) bend

	Phenyl Ring Substitution Overtones	2000-1600(w) - fingerprint region
C-H	Alkynes	3333-3267(s) stretch
		700-610(b) bend
C=C	Alkenes	1680-1640(m,w)) stretch
C□C	Alkynes	2260-2100(w,sh) stretch
C=C	Aromatic Rings	1600, 1500(w) stretch
C-O	Alcohols, Ethers, Carboxylic acids, Esters	1260-1000(s) stretch
C=O	Aldehydes, Ketones, Carboxylic acids, Esters	1760-1670(s) stretch
O-H	Monomeric -- Alcohols, Phenols	3640-3160(s,br) stretch
	Hydrogen-bonded -- Alcohols, Phenols	3600-3200(b) stretch
	Carboxylic acids	3000-2500(b) stretch
N-H	Amines	3500-3300(m) stretch
		1650-1580 (m) bend
C-N	Amines	1340-1020(m) stretch
C-N	Nitriles	2260-2220(v) stretch
NO_2	Nitro Compounds	1660-1500(s) asymmetrical stretch
		1390-1260(s) symmetrical stretch

v - variable, m - medium, s - strong, br - broad, w – weak

4.3 DEDUCTIONS

The following functional groups are certain to be found:

1) Alkanes -2909.09, 2855.13, 1463.50, 1377.43

2) Alkenes-991.93, 965.13, 909.10, 721.50

3) Aldehydes, Ketones, Carboxylic acids, Esters-1712.51, 1641.59

4.4 GAS CHROMATOGRAPHY-MASS SPECTROMETRY (GC-MS)

Gas chromatography-mass spectrometry (GC-MS) is a method that combines the features of gas-liquid chromatography and mass spectrometry to identify different substances within a test sample. Applications of GC-MS include drug detection, fire investigation, environmental analysis, explosives investigation, and identification of unknown samples. GC/MS can also be used in airport security to detect substances in luggage or on human beings. Additionally, it can identify trace elements in materials that were previously thought to have disintegrated beyond identification.

The GC-MS has been widely heralded as a "gold standard" for forensic substance identification because it is used to perform a specific test. A specific test positively identifies the actual presence of a particular substance in a given sample. A non-specific test merely indicates that a substance falls into a category of substances. Although a non-specific test could statistically suggest the identity of the substance, this could lead to false positive identification [10, 11].

4.5 INSTRUMENTATION

The GC-MS is composed of two major building blocks: the gas chromatograph and the mass spectrometer. The gas chromatograph utilizes a capillary column which depends on the column's dimensions (length, diameter, film thickness) as well as the phase properties (e.g. 5% phenyl polysiloxane). The difference in the chemical properties between different molecules in a mixture will separate the molecules as the sample travels the length of the column. The molecules take different amounts of time (called the retention time) to come out of (elute from) the gas chromatograph, and this allows the mass spectrometer downstream to capture, ionize, accelerate, deflect, and detect the ionized molecules separately. The mass spectrometer does this

by breaking each molecule into ionized fragments and detecting these fragments using their mass to charge ratio.

These two components, used together, allow a much finer degree of substance identification than either unit used separately. It is not possible to make an accurate identification of a particular molecule by gas chromatography or mass spectrometry alone. The mass spectrometry process normally requires a very pure sample while gas chromatography using a traditional detector (e.g. Flame Ionization Detector) detects multiple molecules that happen to take the same amount of time to travel through the column (i.e. have the same retention time) which results in two or more molecules to co-elute. Sometimes two different molecules can also have a similar pattern of ionized fragments in a mass spectrometer (mass spectrum). Combining the two processes makes it extremely unlikely that two different molecules will behave in the same way in both a gas chromatograph and a mass spectrometer. Therefore when an identifying mass spectrum appears at a characteristic retention time in a GC-MS analysis, it typically lends to increased certainty that the analyte of interest is in the sample [10, 11].

Fig.4.9 A Typical GC-MS

Table 4.5 A TYPICAL GC-MS ANALYSIS OF THE PRODUCTS OF LDPE PYROLYSIS [12].

Name of compounds	**Percentage area**
Octadecane	1.74
eicosane	4.86
Nonadecane	2.09
Heneicosane	1.6
Hexadecane	1.57
Docosane	1.56
Tetracosane	1.33
Decane	1.35
Dodecane	1.51
Heptadecane	1.59
Pentacosane	1.17
Pentadecane	1.79
Tetradecane	1.66
Tridecane	1.61
Undecane	1.46
Cyclotetracosane	2.06
(1.alpha, 3.alpha, 5.alpha)-1,3,5-trimethyl-cyclohexane	0
2,4-Diethyl-1-methyl-cyclohexane	0
1-Ethyl-2-propyl-cyclohexane	0
1,2,3-Trimethylcyclohexane (1r,2t,3c)	0
1-Ethyl-2,4-dimethyl-cyclohexane	0
1,2-Diethyl-3-methyl-cyclohexane	0
Trans-2-(1-methylethyl)1,10-bicyclohexyl	0
1-Isopropyl-1,4,5-trimethylcyclohexane	0
2,4-Dimethyl-1-heptene	0
4-Methyl-2-undecene	0
1-Hexacosene	0
1-Nonadecene	2.73
1,12-Tridecadiene	1.39
1,15-Hexadecadiene	1.67
1,19-Eicosadiene	4.19
1,21-Docosadiene	2.3
1-Decene	2.87
1-Docosene	1.46
1-Dodecene	2.61
1-Hexadecene	2.88
1-Nonene	2.73
1-Octadecene	3.36
1-Pentadecene	3.02
1-Tetradecene	2.96
1-Tridecene	2.63

2-5-Nonadecene	2.5
3-Heptadecene,(Z)-	3.11
Z-12-pentacosene	2.83
Undecene	2.84
Z-12-pentacosene	2.83
Z-5-nonadecene	8.15
Naphthalene	0.99
2-Phenyl-Naphthalene	0
Biphenyl	0
Acetophenone	0
1-Phenyl-1,2-propanedione	0
4-Methyl-1,10-biphenyl	0
3-(3-methoxyphenyl)-1H-1,2,4-triazole	0
1-(1,10-biphenyl)-4-yl-ethanone	0
Triphenylene	0
m-Terphenyl	0
p-Terphenyl	0
1-terphenyl	0
1’’’-quaterphenyl	0
Anthracene	0
Styrene	1.07
2-Phenyl-5-bezylideneamino-benzimiazole	0
Dibenzoate-1,2-ethanediol	0
Benzoic acid	0
4-Methyl-benzoic acid	0
4-Ethylbenzoic acid	0
4-Acetylbenzoic acid	0
Total area	93.28

4.6 PRECAUTIONS

1) While taking out the reactor after the pyrolysis care must be taken as it is hot and can cause serious burns.

2) The gasket and the condenser are the two most hard to get materials because once ordered they take about 2 weeks to be delivered, special care must be taken for their handing.

3) While performing the experiment the reactor should be sealed properly otherwise there might be a loss of volatile substances.

4) The condenser as well as the measuring cylinder should be cleaned before performing the experiment.

5) Weight of the feed catalyst as well as the products must be taken with care.

CHAPTER 5

RESULTS

RESULTS

1) LDPE pyrolysis takes a long time at temperatures below 500^0C but starts to pick up as we increase the temperature and the amount of catalyst.

2) For thermal as well as catalytic pyrolysis the maximum liquid product yield is seen for 550^0C, the liquid product yield goes on increasing as we increase the temp while we are below 550^0C and decreases after that.

3) The catalyst silica-alumina has a profound effect on the rate of the reaction, in comparison with thermal pyrolysis the liquid product yield is more in the case of catalytic pyrolysis.

4) The yield of liquid product is maximum for the catalyst ratio (1:4) to the LDPE material.

5) An FT-IR study of the product of the product found the predominant presence of alkanes , alkenes,aldehydes,ketones, Carboxylic acids and esteric functional groups which is confirmed by a typical GC-MS analysis of an LDPE pyrolysis product.

CHAPTER 6

CONCLUSION

The pyrolysis of LDPE takes a long time to complete below 500^0C,the yield of liquid product goes on increasing as we increase the temperature and reaches a max at 550^0C, the yield of product is more in the case of catalytic pyrolysis and is maximum for a 4:1 ratio with silica-alumina catalyst at 550^0C.The pyrolysis product is mainly constituted of alkanes, alkenes, aldehydes, ketones and carboxylic acid functional groups.

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